

Preparation of dialkyl-ansa-metallocenes

The present invention relates to a process for the racemoselective preparation of silicon-bridged dialkyl-ansa-metallocenes of the formula (I) and also to the use of a transition metal dialkyl compound of the formula (III) for the racemoselective preparation of these metallocenes.

The preparation of isotactic polypropylene (i-PP) is generally carried out using ansa-metallocenes in their racemic form. Metallocenes which have been found to give particularly good performance and are therefore industrially relevant are substituted silicon-bridged ansa-bisindenylzirconocene dichlorides as described in EP-B 0 485 821, EP-A 0 549 900 or EP-A 0 576 970.

The catalyst system used for the polymerization of olefins usually comprises at least one metallocene and at least one cocatalyst, for example a methylaluminoxane or a borate salt. When using a borate salt, for example $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or $[\text{HN}(\text{n-Bu})_3]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, as cocatalyst, the metallocenes are preferably used as dialkyl-metallocenes. The dialkyl-metallocenes have two alkyl radicals bound to the transition metal.

Processes for synthesizing dialkyl-metallocenes are known. In US patent 5,936,108, metallocene dichlorides such as zirconocene dichlorides are reacted with lithium alkyl compounds such as methyllithium, with the chloride ligands on the transition metal being replaced by alkyl radicals. In EP-A 0 682 036, monomethyl- and dimethyl-metallocenes are synthesized by reaction of the corresponding metallocene dichlorides with trimethylaluminum in the presence of potassium fluoride.

In both processes, the previously synthesized metallocene dichloride is used as starting compound, so that the synthesis of racemic dimethyl-metallocenes requires the corresponding racemic metallocene dichlorides as starting compounds. However, the synthesis of the corresponding ansa-metallocene dichlorides usually gives them as a rac/meso mixture, so that the meso compound has to be separated off.

Journal of Organometallic Chemistry 535 (1997) 29-32 describes a process for the synthesis of variously bridged dimethyl-bisindenylzirconocenes which bear hydrogen in each of the 2 positions of the two indenyl radicals. In this process, the doubly deprotonated bridged bisindenyl ligand is reacted with dimethylzirconium dichloride, which has to be handled at below -40°C . In the case of the synthesis of dimethylsilylbisindenyl dimethylzirconium, which bears hydrogen atoms in the 2 positions on the two indenyl radicals, a meso-enriched product mixture was obtained, so that the meso product, which is here the main product, would have to be separated off to obtain the rac isomer.

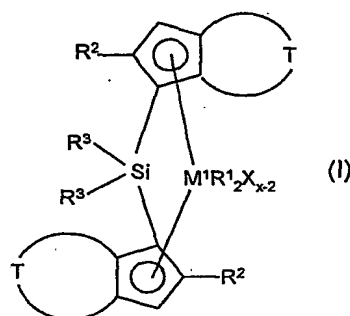
For the abovementioned reasons, the known methods of preparing racemic silicon-bridged dialkyl-ansa-metallocenes leave something to be desired in respect of economics and ability to be readily implemented in industry.

5

It is an object of the present invention to find a process for preparing predominantly racemic silicon-bridged dialkyl-ansa-metallocenes which offers advantages both from an economic point of view and also in terms of ability to be implemented in industrial production.

10. We have found that this object is achieved by a process for the racemoselective preparation of silicon-bridged dialkyl-ansa-metallocenes of the formula (I)

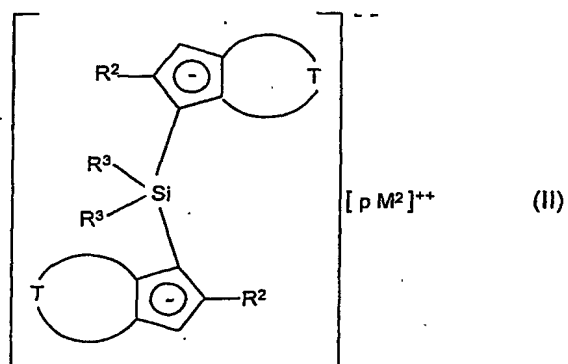
15



20

which comprises reacting a ligand starting compound of the formula (II)

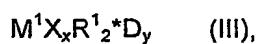
25



30

with a transition metal dialkyl compound of the formula (III)

35



40

where

M^1 is an element of group 4, 5 or 6 of the Periodic Table of the Elements,

5 R^1 are identical C_1 - C_{20} -alkyl or C_7 - C_{40} -arylalkyl radicals,

X are identical or different halogens,

10 R^2 are identical or different C_1 - C_{40} radicals,

R^3 are identical or different C_1 - C_{40} radicals,

15 T is a divalent C_1 - C_{40} group which together with the cyclopentadienyl ring forms a further saturated or unsaturated ring system which has a ring size of from 5 to 12 atoms, where T may contain the heteroatoms Si, Ge, N, P, O or S in the ring system fused onto the cyclopentadienyl ring,

M^2 is Li, Na, K, MgCl, MgBr, MgI, Mg or Ca,

20 D is an uncharged Lewis base ligand,

x is equal to the oxidation number of M^1 minus 2,

25 y is from 0 to 2

and

30 p is 1 in the case of doubly positively charged metal ions or 2 in the case of singly positively charged metal ions or metal ion fragments.

Furthermore, the use of the transition metal dialkyl compound of the formula (III) for the racemoselective preparation of silicon-bridged dialkyl-ansa-metallocenes of the formula (I) has been found.

35 M^1 is an element of group 3, 4, 5 or 6 of the Periodic Table of the Elements or of the lanthanides, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum or tungsten, preferably titanium, zirconium or hafnium, particularly preferably zirconium or hafnium and very particularly preferably zirconium.

The radicals R^1 are identical and are each C_1 - C_{20} -alkyl, preferably C_1 - C_5 -alkyl, or C_7 - C_{40} -arylalkyl, preferably C_7 - C_{15} -arylalkyl, where the aryl part contains from 6 to 10, preferably 6, carbon atoms and the alkyl part preferably contains 1 carbon atom and the aryl part may be substituted by further C_1 - C_4 -alkyl radicals. The radicals R^1 are particularly preferably methyl or benzyl, in particular methyl.

The radicals X are identical or different, preferably identical, and are each halogen, for example fluorine, chlorine, bromine or iodine, preferably chlorine.

- 10 The radicals R^2 are identical or different and are each a C_1 - C_{40} radical which is preferably bound via a carbon atom to the cyclopentadienyl ligand and may be branched in the α position or unbranched. R^2 is preferably a linear or branched C_1 - C_{20} -alkyl radical, preferably a C_1 - C_8 -alkyl radical, particularly preferably a C_1 - C_4 -alkyl radical, or an arylalkyl radical having from 1 to 10, preferably from 1 to 4, carbon atoms in the alkyl part and from 6 to 22, preferably from 6 to 10, carbon atoms in the aryl part. Examples of very particularly preferred radicals R^2 are methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, n-pentyl, n-hexyl, benzyl and 2-phenylethyl.

- Unless restricted further, alkyl is a linear, branched or cyclic radical such as methyl, ethyl, n-propyl, isopropyl, n-butyl, i-butyl, s-butyl, t-butyl, n-pentyl, cyclopentyl, n-hexyl, cyclohexyl, n-heptyl or n-octyl.

- The radicals R^3 are identical or different and are each a C_1 - C_{40} radical, for example a C_1 - C_{20} -alkyl radical, preferably a C_1 - C_4 -alkyl radical, a C_2 - C_{20} -alkenyl radical, preferably a C_2 - C_4 -alkenyl radical, a C_6 - C_{22} -aryl radical, preferably a C_6 - C_{10} -aryl radical, an alkylaryl or arylalkyl radical having from 1 to 10, preferably from 1 to 4, carbon atoms in the alkyl part and from 6 to 22, preferably from 6 to 10, carbon atoms in the aryl part, where the radicals may also be halogenated. Examples of particularly preferred radicals R^3 are C_1 - C_4 -alkyl, in particular methyl or ethyl, and phenyl.

- 30 T is a divalent C_1 - C_{40} group which together with the cyclopentadienyl ring forms a further saturated or unsaturated ring system which has a ring size of from 5 to 12, preferably from 5 to 7, particularly preferably 5 or 6, atoms, where T may contain the heteroatoms Si, Ge, N, P, O or S, preferably N or S, in the ring system fused onto the cyclopentadienyl ring.

- 35 M^2 is preferably Li, MgCl, MgBr or Mg, in particular Li.

The uncharged Lewis base ligand D can, for example, be a linear, cyclic or branched oxygen-, sulfur-, nitrogen- or phosphorus-containing, preferably oxygen-containing, hydrocarbon. Preference is given to ethers and polyethers such as diethyl ether, dibutyl ether, tert-butyl methyl

ether, anisole, triglyme, tetrahydrofuran and dioxane. Particular preference is given to 1,2-dimethoxyethane and tetrahydrofuran.

Particular preference is given to a process for the racemoselective preparation of silicon-bridged
5 dialkyl-ansa-metallocenes of the formula (I),

in which

- 10 T is a 1,3-butadiene-1,4-diyl group which may be unsubstituted or be substituted by from 1 to 4 radicals R^4 , where the two 1,3-butadiene-1,4-diyl groups may be different,
- R^4 are identical or different C_1 - C_{20} radicals,
- 15 M^1 is titanium, zirconium or hafnium,
- R^1 are identical C_1 - C_5 -alkyl or C_7 - C_{20} -arylalkyl radicals,
- X is halogen and
- 20 R^2 , R^3 , M^2 , D, p, x and y are as defined above.

Preference is given to M^1 being zirconium and R^1 being methyl.

25 The 1,3-butadiene-1,4-diyl groups T are identical or different, preferably identical.

The radicals R^4 on the substituted 1,3-butadiene-1,4-diyl groups T are identical or different, in particular identical, and are each a C_1 - C_{20} radical such as a C_1 - C_4 -alkyl radical or a substituted or unsubstituted C_6 - C_{40} -aryl radical. The radicals R^4 are particularly preferably substituted or
30 unsubstituted C_6 - C_{40} -aryl radicals having from 1 to 10, preferably from 1 to 4, carbon atoms in the alkyl part and from 6 to 22, preferably from 6 to 10, carbon atoms in the aryl part, where the radicals may also be halogenated. Examples of preferred radicals R^4 are phenyl, 2-tolyl, 3-tolyl, 4-tolyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 3,5-di(tert-butyl)phenyl, 2,4,6-trimethylphenyl, 2,3,4-
35 trimethylphenyl, 1-naphthyl, 2-naphthyl, phenanthrenyl, p-isopropylphenyl, p-tert-butylphenyl, p-s-butylphenyl, p-cyclohexylphenyl and p-trimethylsilylphenyl.

The number of radicals R^4 on the substituted 1,3-butadiene-1,4-diyl groups T is preferably 1 or 2, in particular 1.

The 1,3-butadiene-1,4-diyl group T together with the cyclopentadienyl radical forms an indenyl system which is, in particular, substituted in the 2,4 positions, 2,4,5 positions, 2,4,6 positions or 2,4,7 positions, where two substituents on the six-membered ring of the indenyl system may
5 together be part of a further ring system, for example a further 1,3-butadiene-1,4-diyl group. The indenyl systems are very particularly preferably substituted in the 2,4 positions.

The substitution pattern indicated in the example of the process of the present invention is most preferred.

10

In the process of the present invention, the salt-like ligand starting compounds of the formula (II) are prepared either in isolated form in situ immediately before the reaction with the transition metal dialkyl compound of the formula (III).

15 To synthesize the salt-like ligand starting compounds of the formula (II), the corresponding uncharged silicon-bridged biscyclopentadienyl compound is doubly deprotonated by means of a strong base. Strong bases which can be used are, for example, organolithium or organomagnesium compounds such as methyllithium, n-butyllithium, sec-butyllithium, n-butyl-n-octylmagnesium or dibutylmagnesium.

20

The uncharged silicon-bridged biscyclopentadienyl compound to be deprotonated can once again be used in isolated form or without isolation directly from the bridging reaction of two cyclopentadienyl anions with an appropriate silicon reagent, for example a diorganodichlorosilane such as dimethyldichlorosilane. A further possible way of preparing the uncharged silicon-bridged
25 biscyclopentadienyl compounds is a stepwise route. In this case, for example, a cyclopentadienyl anion is reacted with an appropriate silicon reagent, for example a diorganodichlorosilane such as dimethyldichlorosilane, to form a monochloromonocyclopentadienyldiorganosilane compound and the chlorine in this is subsequently replaced by a further cyclopentadienyl group, which may be different from the first, to obtain the desired uncharged silicon-bridged biscyclopentadienyl
30 compound.

The synthesis of the cyclopentadienyl anions can in principle be carried out under the same conditions as the deprotonation of the uncharged silicon-bridged biscyclopentadienyl compound.

35 The double deprotonation of the uncharged silicon-bridged biscyclopentadienyl compound to form the ligand starting compound of the formula (II) is usually carried out in the temperature range from -78°C to 110°C , preferably from 0°C to 80°C and particularly preferably from 20°C to 60°C .

40

Suitable inert solvents in which the deprotonation of the cyclopentadienyl derivatives by means of strong bases can be carried out are aliphatic or aromatic hydrocarbons such as benzene, toluene, xylene, mesitylene, ethylbenzene, cumene, decalin, tetralin, pentane, hexane, cyclohexane or heptane or ethers such as diethyl ether, di-n-butyl ether, tert-butyl methyl ether (MTBE), tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), anisole, triglyme or dioxane and also any mixtures of these materials. Preference is given to solvents or solvent mixtures in which the subsequent process of the present invention for preparing the metallocene complexes of the formula (I) can likewise be carried out.

10 In an embodiment of the process of the present invention, the transition metal dialkyl compound of the formula (III) is produced at above -30°C , in particular above 0°C , by combining a compound M^1X_{x+2} with from 2 to 2.5 equivalents of a compound R^1M^3 in the presence of a ligand compound D, where

15 M^3 is Li^+ , Na^+ , K^+ , MgCl^+ , MgBr^+ , MgI^+ , $\frac{1}{2} [\text{Mg}^{++}]$ or $\frac{1}{2} [\text{Zn}^{++}]$, and

the other variables are as defined above.

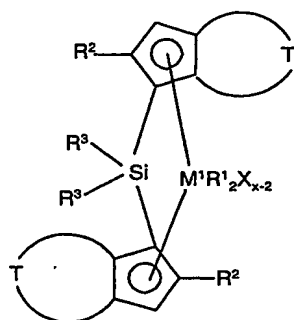
In another embodiment of the process of the present invention, the ligand starting compound of the formula (II) is combined with the transition metal dialkyl compound of the formula (III) at above -30°C , preferably above 0°C .

After the reaction components have been combined, the reaction mixture is preferably maintained at from 30°C to 150°C , in particular from 50°C to 80°C , for a period of at least 10 minutes, preferably from 1 to 8 hours.

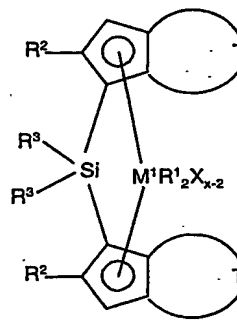
In a further embodiment of the process of the present invention, the reaction is carried out in an organic solvent or solvent mixture which comprises at least 10% by volume, preferably at least 50% by volume, particularly preferably at least 80% by volume, very particularly preferably at least 90% by volume, of an ether, in particular a cyclic ether. An example of a very useful ether is tetrahydrofuran. Further inert solvents which may be present in the reaction solution are the abovementioned aliphatic or aromatic hydrocarbons or ethers in which the deprotonation of the ligand can be carried out.

35 In the process of the present invention, it is possible for not only the desired rac compounds of the formula (I) but also the corresponding meso compounds to be formed. In those cases in which the two cyclopentadienyl radicals on the silicon bridge are not identical, the compound does not exist in a meso form having C_s symmetry or rac form having C_2 symmetry, but instead there are only diastereomeric compounds having C_1 symmetry. In cases in which the two cyclopentadienyl

radicals are identical but the two radicals R^3 on the silicon bridge are not identical, the compound exists as a racemic diastereomer having C_1 symmetry and two different meso diastereomers having C_s symmetry. When used as catalyst components in the polymerization of propylene, these different diastereomeric metallocene compounds which differ from one another in the three-dimensional arrangement of the various substituents behave, solely on the basis of the three-dimensional arrangement of the two cyclopentadienyl ligands relative to one another, like the C_2 -symmetric rac isomers (isotactic polypropylene) or like the C_s -symmetric meso isomer (atactic polypropylene) and can thus each be designated as a pseudo-rac form or a pseudo-meso form.



(I)
rac or pseudo-rac



(Ia)
meso or pseudo-meso

In the following, rac and pseudo-rac form and meso and pseudo-meso form will be differentiated only as rac form and meso form.

In a further embodiment of the process of the present invention, the racemoselectivity = (proportion of rac – proportion of meso)/(proportion of rac + proportion of meso) is greater than zero, preferably greater than 0.5.

The invention further provides for the use of the transition metal dialkyl compound of the formula (III) for the racemoselective preparation of silicon-bridged dialkyl-ansa-metallocenes of the formula (I) as described above.

Illustrative but nonlimiting examples of metallocenes of the formula (I) are:

dimethylsilanediylbis(2-methyl-4-phenylindenyl)dimethylzirconium,
dimethylsilanediylbis(2-methyl-4,5-benzoidenyl)dimethylzirconium,
dimethylsilanediylbis(2-methyl-4-(4'-tert-butylphenyl)indenyl)dimethylzirconium,
dimethylsilanediylbis(2-ethyl-4-(4'-tert-butylphenyl)indenyl)dimethylzirconium,
dimethylsilanediylbis(2-n-propyl-4-(4'-tert-butylphenyl)indenyl)dimethylzirconium,
dimethylsilanediyl(2-methyl-4-(4'-tert-butylphenyl)indenyl)(2-isopropyl-4-(4'-tert-butylphenyl)indenyl)dimethylzirconium,

dimethylsilanediyl(2-ethyl-4-(4'-tert-butylphenyl)indenyl)(2-isopropyl-4-(4'-tert-butylphenyl)indenyl)dimethylzirconium,

dimethylsilanediyl(2-methyl-4-phenylindenyl)(2-isopropyl-4-(4'-tert-butylphenyl)indenyl)dimethylzirconium,

- 5 dimethylsilanediyl(2-isopropyl-4-(4'-tert-butylphenyl)-1-indenyl)(2,7-dimethyl-4-(4'-tert-butylphenyl)indenyl)dimethylzirconium,
dimethylsilanediyl(2-isopropyl-4-(4'-tert-butylphenyl)-1-indenyl)(2-ethyl-7-methyl-4-(4'-tert-butylphenyl)indenyl)dimethylzirconium.

- 10 The salts of the formula M^2X or M^2X_2 , for example lithium chloride or magnesium chloride, which are obtained as coproduct in the process of the present invention for preparing racemic silicon-bridged dialkyl-ansa-metallocenes of the formula (I) can be separated off from the metallocene by known methods. For example, a salt such as lithium chloride can be precipitated by means of a suitable solvent in which the metallocene, however, is soluble, so that the solid lithium chloride is
15 separated off from the dissolved metallocene by means of a filtration step. The metallocene can also be separated off from the salt by extraction with a suitable solvent of this type. Any such filtration steps can also be carried out using filter aids such as kieselguhr. For example, organic solvents, in particular organic aprotic, oxygen-free solvents such as toluene, ethylbenzene, xylenes or methylene chloride, can be used for such a filtration or extraction step. If necessary,
20 the solvent components in which the salt is at least partly soluble are removed to a substantial extent before the salt is separated off as described above. For example, lithium chloride is appreciably soluble in tetrahydrofuran.

- The racemic silicon-bridged dialkyl-ansa-metallocenes of the formula (I) prepared by the process
25 of the present invention are used as catalyst constituents together with suitable cocatalysts and, if appropriate, suitable support materials in the catalyst systems for the homopolymerization or copolymerization of α -olefins.

30

35

40

Examples:

General

All experiments using organometallic compounds were carried out in baked glass vessels and
5 under a protective argon atmosphere.

1 Synthesis of $\text{Me}_2\text{Si}(2\text{-Me-4-PhInd})_2\text{ZrMe}_2$

1a Synthesis of dimethylzirconium dichloride (1)

10 356 ml of THF were placed in a reaction vessel at 0°C and 4.97 g of zirconium tetrachloride (21.3 mmol) were added. At 0°, 47 ml of 1M methyllithium solution in cumene/THF (47 mmol = 2.2 eq) were added dropwise over a period of 8 minutes. The yellow solution was subsequently stirred for another 30 minutes at 0°C.

15 1b Synthesis of $\text{Me}_2\text{Si}(2\text{-Me-4-PhInd})_2\text{ZrMe}_2$ (2)

10 g of dimethylbis(2-methyl-4-phenyl-1-indenyl)silane (21.3 mmol) were dissolved in 236 ml of THF, cooled to 0°C and 18.8 ml of butyllithium solution (2.5 molar in toluene, corresponding to 47 mmol = 2.2 eq) were added dropwise over a period of 4 minutes. The cold bath was removed and the reaction mixture was stirred for another 25 minutes ($T = 15^\circ\text{C}$). The reddish brown
20 reaction mixture was added at 0°C to the solution of dimethylzirconium dichloride prepared in Experiment 1a over a period of 15 minutes and the resulting mixture was subsequently heated to 65°C.

After 4.5 hours at 65°C, about 90% of the solvent (596 ml) were distilled from the brown suspension. The proton NMR of a sample of the crude product indicated a rac/meso ratio of
25 3 : 1. 375 ml of toluene were subsequently added to the crude product suspension and the suspension was stirred at 60°C for 30 minutes, filtered through a G3 protective gas frit and the residue was washed once with 50 ml of warm toluene (60°C).

The filtrate was evaporated to about ¼ of its volume (125 ml) and the solid formed was filtered off via a G3 protective gas frit. The yellowish green residue was washed twice with 3 ml of
30 toluene and dried in an oil pump vacuum.

Yield: 3.86 g of (2) as a yellow solid; pure rac isomer according to proton NMR (corresponds to 31% of the theoretical yield)